

## **Dispersion of Functionalized Nanoclay Platelets in an Amine-Cured Epoxy Resin System**

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### **ABSTRACT**

Nanocomposites are a relatively new class of materials obtained by dispersing montmorillonite clay in a polymer matrix. Evidences from literature suggest that clay platelet dispersion during nanocomposite preparation and clay-matrix adhesion are major technical issues that need to be addressed in order to achieve the desired property enhancements in polymer-clay hybrid nanocomposites. We have studied the interaction of the organically functionalized clay with the epoxy resin by including along the chain structure functional groups that will facilitate interaction with the resin. Through conventional routes, functional molecules have been synthesized and deposited on to the clay surface. Both the functionalized and nonfunctionalized clay has been analyzed using thermal gravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR). The exfoliation of nanoclay platelets in amine cured epoxy system has been studied using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

### **INTRODUCTION**

Aromatic amine cured epoxy resins, where the diglycidyl ether of bisphenol-A (DGEBA) resin cured with meta-phenylene diamine (MPDA) is a representative member, are the most widely used matrix materials for preparing conventional composites. Resins of this class are brittle and their ability to absorb energy during failure is limited. The successful use of nanoclay reinforcement technology to improve the performance of epoxy resin would represent a major technical achievement in the development of high-temperature and tough advanced structural materials. Nanoclays are inexpensive relative to traditional reinforcing materials, thermally inert, and environmentally friendly. The use of nanoclay hybrid polymer composites in structural parts is expected to improve environmental and moisture stability and increase energy efficiency in the transportation sector through weight reduction [1].

Evidences from literature suggest that exfoliation and dispersion of clay platelets during nanocomposite preparation and clay-matrix adhesion are major issues that needs to be addressed in order to achieve the desired property enhancements in polymer-clay nanocomposites [2-7]. In recent years, efforts have focussed on understanding the nature and mechanism of the exfoliation process of the surface treated clay in the polymer network structure. For example, Messersmith and Giannelis [2] achieved a significant increase in stiffness of epoxy nanocomposite by using organoclays modified with bis(2-hydroxyethyl) methyl tallow-alkyl ammonium chloride at a mass fraction of 4 %. The role of the organic chain on alkyl ammonium chloride is primarily to facilitate the intercalation of the clay by organic molecules (e.g., DGEBA). These researchers found that curing of a DGEBA/clay mixture with primary and secondary amines resulted in an

immediate clouding of the resin. It has been suggested that the bridging of the silicate layers by the bifunctional polar amines prevented the extensive layer separation. In recent years, several researchers [2-7] have studied amine-cured epoxy clay composites to show that exfoliation of nanocomposite depends on the following parameters:

- (1) Alkyl ammonium ion type (e.g. primary, secondary or tertiary)
  - a. affects intra-gallery polymerization rates and clay-matrix dispersion
- (2) Length of the alkyl chain
  - a. impacts swelling of clay by epoxy monomer
  - b. controls intra-gallery diffusion
- (3) Curing agent type (e.g. aromatic diamines, aliphatic diamines, anhydrides, and homopolymerization agents)
  - a. affects resin glass transition temperature
- (4) Curing conditions
  - a. affects intra- and extra-gallery polymerization rates and resin T<sub>g</sub>
- (5) Charge density of the clay
  - a. impacts swelling of clay by epoxy monomer

The focus of this research is to investigate the influence of modified clay with functional groups on the miscibility of monomer with organically modified nanoclay platelets. In this research, the sodium ions in the clay are exchanged with an alkylammonium salt of suitable chain length followed by adsorption of  $\omega$ -epoxy carboxylic acid of suitable chain length on the clay surface. The epoxy groups of  $\omega$ -epoxy carboxylic acid are expected to facilitate the miscibility of DGEBA monomer with the clay platelets. In this study we investigate how the type of organophilic groups intercalated between the clay layers, influences the structure of the resulting nanocomposites. In particular, we compare the effect of the two nanoclays (functional and non-functional clay) on the exfoliation process and the final structure of epoxy-based nanocomposites. For the synthesis of functional clay, we use clay treated with C18 quaternary ammonium salts (C18 clay) as the base structure. The C18 clay is then mixed with *functional oleochemicals* to form functional clays. The functional oleochemicals are synthesized from vernonia oil (see Figure 1). The nanostructure of the epoxy clay composite was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

## EXPERIMENTAL

### (A) Synthesis of C18 Clay

7.5 g of purified Na clay from Southern Clay Products<sup>1</sup> was dispersed into 600 ml of distilled water at 80 °C. 3.0 g of octadecylammonium chloride in 300 ml distilled water was poured in the hot clay/water suspension and stirred vigorously for 1 h at 80 °C. The mixture was then filtered and the solid washed several times with ethanol/hot water mixture (for 3 h) to remove free chloride ions. The washing was continued until the solid was verified for absence of chloride ions, by checking the filtrate solution with AgNO<sub>3</sub> solution. The attachment of long alkyl groups to clay surfaces facilitates clay sheet separation and makes it possible to introduce functional molecules in the interlayer space.

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<sup>1</sup> Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily that the items are best suited for the purpose.

**(B) Synthesis of Vernolic acid:**

Vernonia oil (VO) was refluxed with base/methanol mixture for 2 h and transferred to a beaker containing ice/water. The solid compound was recovered by filtration and acid treated to convert the acid salt (soap) to vernolic acid. Vernolic acid was purified by adopting solvent exchange procedure and freeze drying techniques. Figure 1 describes the reaction scheme used to synthesize vernolic acid. The purified compound was FTIR characterized and compared to the literature reporting for epoxy fatty acid [8].

**(C) Synthesis of Vernolic Acid Mixed C18 Clay:**

1.25 g of C18 clay was suspended in 0.5 g of vernolic acid dissolved in 30 ml of hexane and the solution was stirred under nitrogen gas for 48 h and the product was filtered. Fresh hexane was added to the solid product and attempts were made to free the solid product of residual vernolic acid. The C18 clay containing vernolic acid was allowed to air dry and is termed as the *vernolic acid mixed C18 clay*. The product was characterized by FTIR and TGA technique.

**(D) Synthesis of Epoxy Nanocomposite:**

We have selected the model resin system DGEBA (provided by Dow Chemical) and MPDA for the current study. DGEBA resin was kept in a vacuum oven at 75 °C for 3 h. The clay-epoxy mixture was prepared by dispersing a mass fraction of 2.5 % of C18 clay in hot DGEBA with stirring, followed by sonication for about 2 h and degassing in vacuum for 2 h. 14.5 phr MPDA (melted at 60 °C) was then added to the clay-epoxy mixture at 60 °C under vacuum. The DGEBA/clay/MPDA mixture was heated for 2 h at 80 °C and post cured for another 2 h at 125 °C. The same curing procedure was applied to vernolic acid mixed C18 clay.

**(E) FTIR and TGA Analysis of Nanoclay Powder**

FTIR analyses were performed on the Na clay, C18 clay, and vernolic acid mixed C18 clay. Each sample was mixed with KBr and vacuum packed to obtain pellets of the material. The pellets were analyzed using a Nicolet Magna IR 560 (the standard instrument uncertainty in measuring wave number is  $\pm 0.01 \text{ cm}^{-1}$ , the  $\text{cm}^{-1}$  were rounded off to the nearest  $1 \text{ cm}^{-1}$ ) spectrophotometer.

TGA analysis was performed on the Na clay, C18 clay, and vernolic acid mixed C18 clay using a Perkin Elmer 7 Series system (the standard instrument uncertainty in measuring a temperature is  $\pm 1 \text{ }^\circ\text{C}$ ) in a nitrogen atmosphere, by placing 25 mg of sample in a crucible and heating it from 30 °C to 900 °C at a heating rate of 20 °C /min. Nitrogen gas was allowed to flow at a sweep rate of 5 ml/min.

**(F) XRD and TEM Analysis of Epoxy Nanocomposites**

XRD analyses were performed using a Scintag Inc. XRG 3000 diffractometer with Cu radiation (40 KV, 35 mA). The scanning speed and the step size were  $0.01 \text{ }^\circ/\text{min}$  and  $0.04 \text{ }^\circ$ ,

respectively. The nanocomposite dogbone produced during the moulding process has a fairly smooth surface. The dogbone specimens were cut to size and analyzed by XRD.

TEM specimens were cut from dogbone using an ultramicrotome, equipped with a diamond knife. They were collected in a trough filled with water and lifted out of water using 200 mesh copper grids. Electron micrographs were taken with a Philips EM400C at an accelerating voltage of 120 KV.

## RESULTS AND DISCUSSION

### A. Characterization of Nanoclay Powder

The FTIR spectra of the neat Na clay, C18 clay and vernolic acid mixed C18 clay in the region (4000 to 500)  $\text{cm}^{-1}$  are shown in Figure 2. Both the vernolic acid mixed C18 clay and C18 clay display sharp methylene-stretching modes at 2920  $\text{cm}^{-1}$  and 2860  $\text{cm}^{-1}$ , that is characteristic of organophilic groups on clay surfaces. The spectra of C18 and vernolic acid mixed C18 clay also show a distinct peak at 1600  $\text{cm}^{-1}$  that can be assigned to the quaternary ammonium salt in modified clay. In addition, the vernolic acid mixed C18 clay contains bands at 1710  $\text{cm}^{-1}$  and 1759  $\text{cm}^{-1}$  suggesting that the vernolic acid is present in the clay matrix. Vernolic acid present in the interlayer space is trapped in the matrix, while vernolic acid present at the edges in a limited amount is involved in physico-chemical interactions with hydroxyl groups on clay edges. This is because, plate-like clay surfaces have hydroxyl groups at low content at edges of individual particles.

Thermogravimetric analysis was used to examine the stability of organophilic groups on nanoclay. The thermograms of the Na clay, C18 clay, and vernolic acid mixed C18 clay are shown in Figure 3. The peak at 100 °C corresponds to the loss of surface water molecule from the clay platelets. We see the onset of decomposition peak (i.e. release of functional onium ion and vernolic acid molecule) at above 200°C in both C18 and vernolic acid mixed C18 clay. The peak at 650 °C is the irreversible dehydroxylation peak for clay. As expected, the peak at 650°C for Na clay is significantly larger than that of vernolic acid mixed C18 clay.

### B. Characterization of Epoxy Clay Nanocomposites

Both the uncured and cured epoxy were studied by XRD for layer separation. The X-ray diffraction results of C18 clay and vernolic acid mixed C18 clay showed a sharp X-ray diffraction peak that corresponds to a layer separation of about  $(22 \pm 3) \approx$ , where the number after  $\pm$  is one standard deviation from the mean. After the C18 clay was sonicated in epoxy mixture for 2 h, X-ray diffraction was recorded for the uncured sample. The interlayer spacing increased to  $(37 \pm 3) \approx$ . However, when the clay was allowed to swell for several hours in hot epoxy resin, the sharp peak diminished. Instead a shoulder was noticed for both C18 clay and mixed nanoclay. Figure 4 shows a comparison of the C18 clay and vernolic acid mixed C18 clay epoxy nanocomposite. The appearance of a shoulder at approximately  $2.3^\circ$  ( $2\theta$ ) suggests that nanoclay platelets are partially exfoliated. It has been reported recently that epoxy infiltration into nanoclay platelets can be achieved by prolonged swelling of clay in uncured epoxy [10].

To verify our results, we performed TEM studies on C18 clay and vernolic acid mixed C18 clay nanocomposites. Figure 5 shows bright field transmission electron micrograph of epoxy- (a) C18 clay and (b) vernolic acid mixed C18 clay nanocomposite. Detailed TEM

verified the intercalated structure of epoxy C18 clay nanocomposite and partially exfoliated epoxy vernolic acid mixed C18 clay nanocomposite. There were regions in the vernolic acid mixed C18 clay epoxy nanocomposite where the nanoclay platelets were intercalated (regular arrangement of clay platelets) and other regions where platelets were exfoliated (randomly arranged and well separated platelets). One would expect that the addition of vernolic acid to C18 clay should result in intercalated epoxy nanocomposite because of crowding of functional groups on clay edges. However, our preliminary results indicate that the addition of vernolic acid to C18 clay has improved exfoliation of nanoclay platelets to a limited extent in epoxy matrix. We believe that the epoxy groups of  $\omega$ -epoxy vernolic acid sorbed on clay edges may facilitate the miscibility of DGEBA monomer with the clay platelets and infiltration of epoxy resin. This aspect requires further investigation. Studies are also underway to obtain information about the clay dispersability in epoxy matrix (using NMR technique).

## ACKNOWLEDGMENTS

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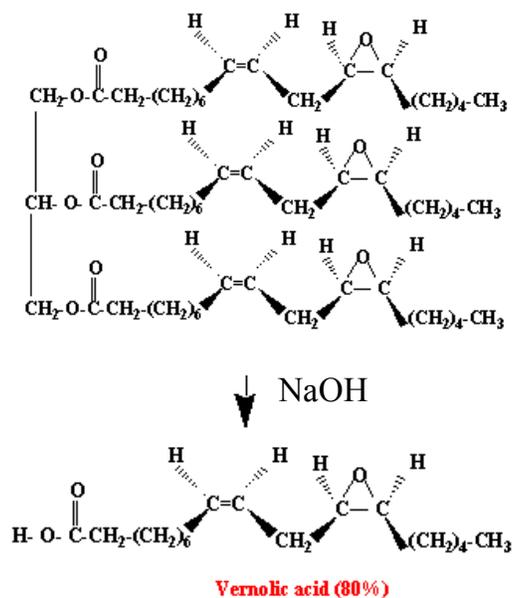


Figure 1. Reaction scheme for vernolic acid

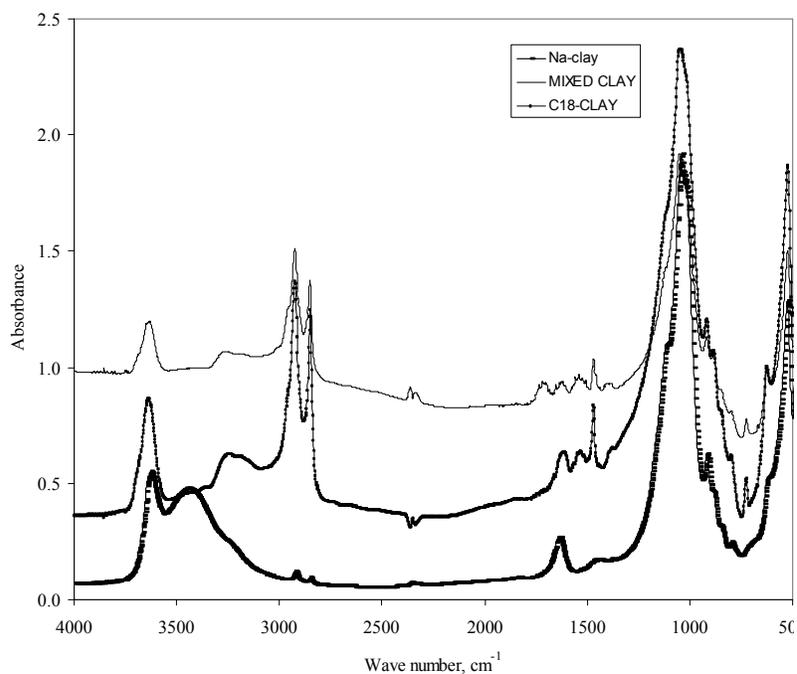


Figure 2. FTIR spectrum of Na-clay, C18 clay and vernolic acid mixed C18 clay powders.

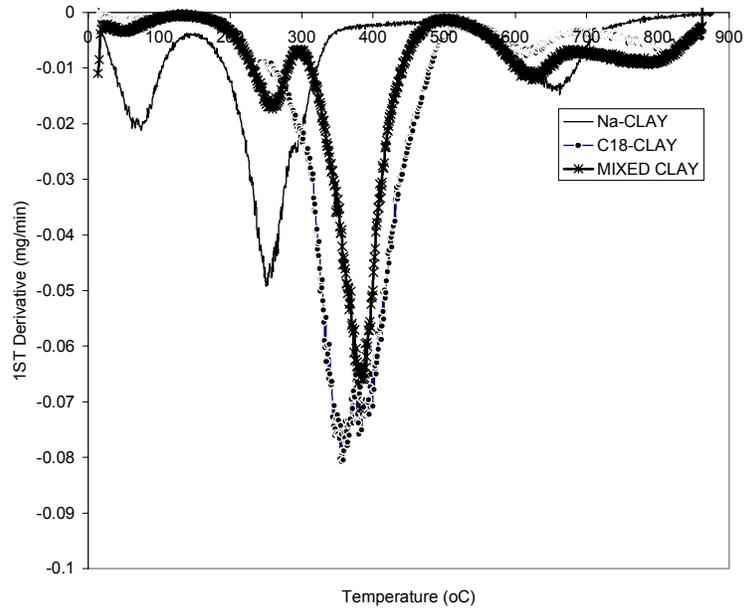


Figure 3 TGA of Na clay, C18 clay and vernolic acid mixed C18 clay powders.

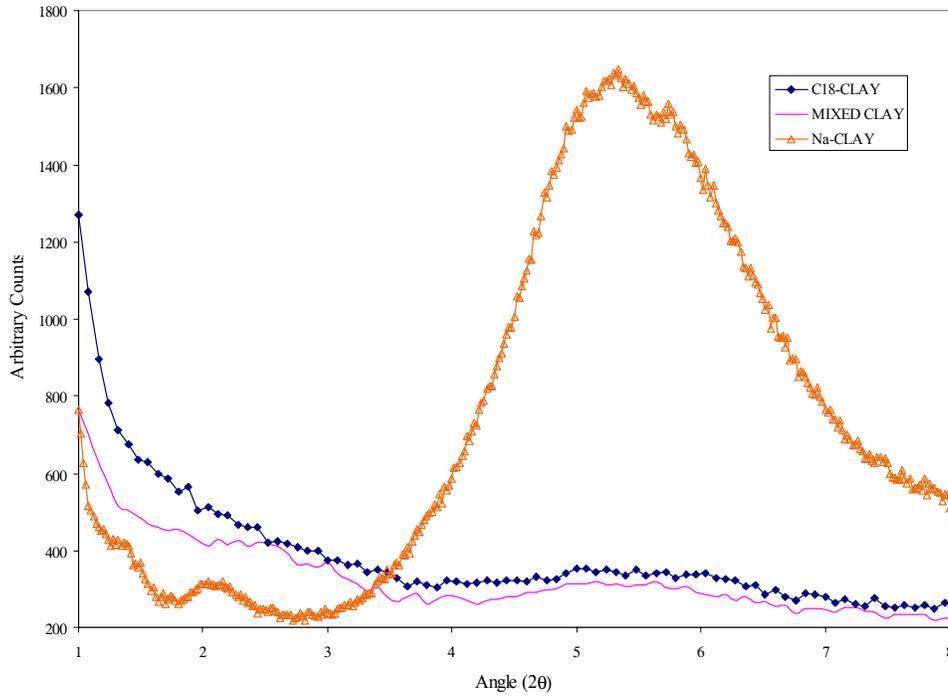
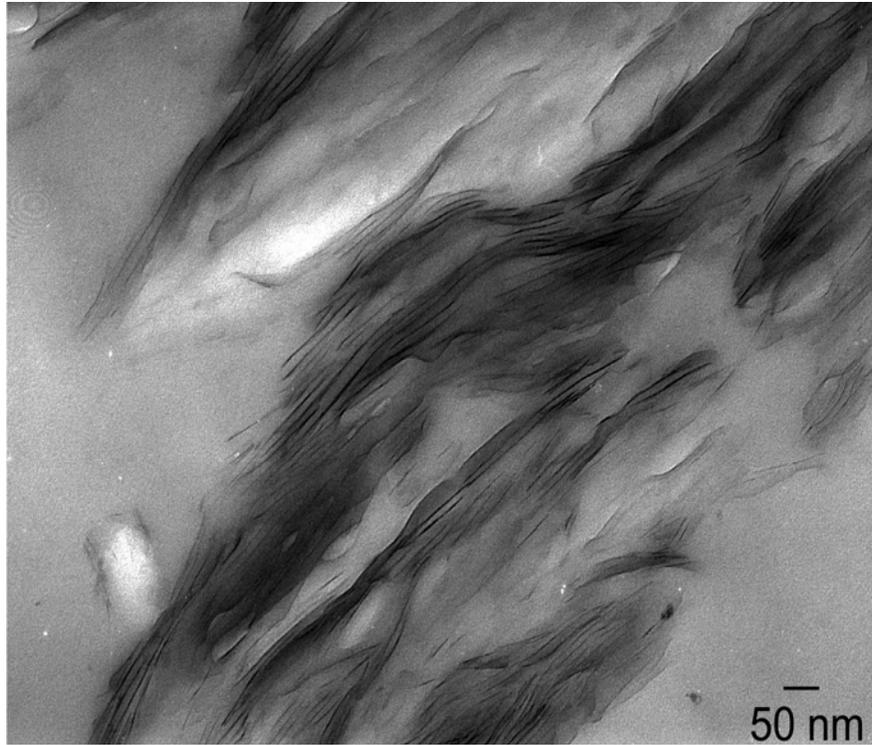
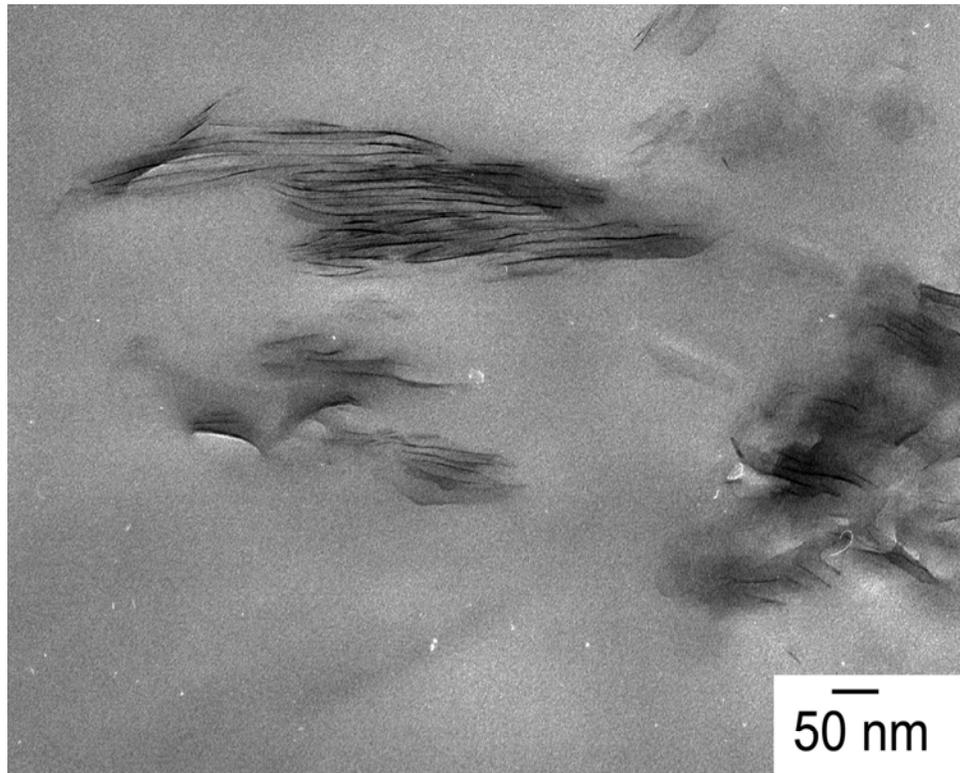


Figure 4. XRD of Na clay, C18 clay and vernolic acid mixed C18 clay nanocomposite.



a



b

Figure 5. TEM of (a) vernolic acid mixed C18 clay and (b) C18 clay nanocomposite (the standard uncertainty of magnification is 3 %).